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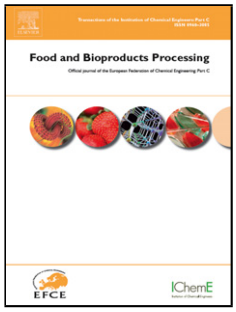

Thermal processing of raspberry pulp: effect on the color and bioactive compounds

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Thermal processing of raspberry pulp: effect on the color and bioactive compounds.

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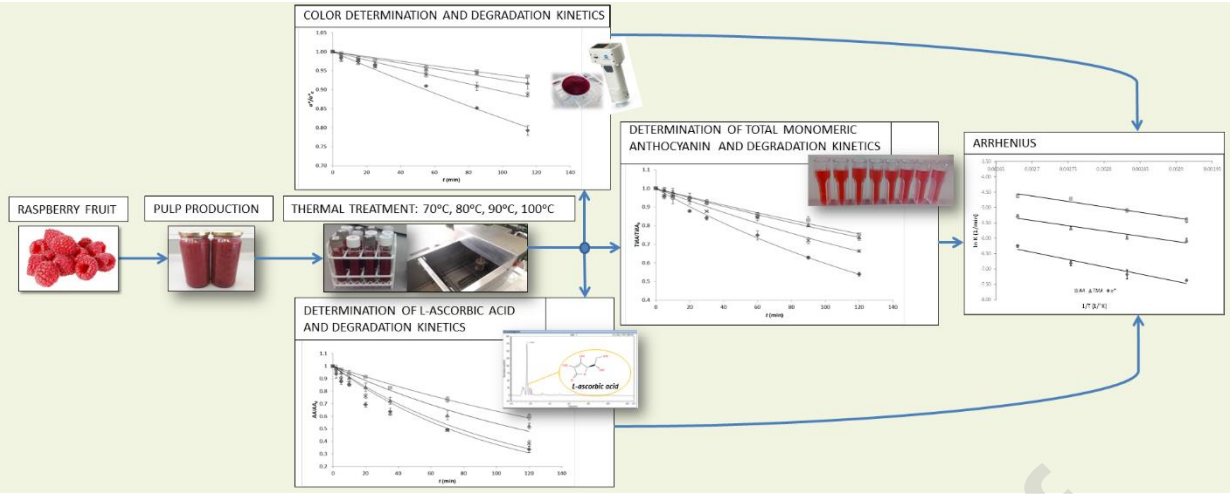
Graphical abstract



Highlights

- Impact of heating on physio-chemical properties of raspberry pulp was studied
- Color, TMA and AA degradations followed first order kinetic and Arrhenius models
- BI was the most susceptible parameter to temperature changes
- AA presented the highest degradation rate for all temperatures studied
- The degradation of total anthocyanins showed a strong positive correlation with *a**

Abstract

The effect of heating on color degradation and the bioactive compounds, such as total monomeric anthocyanins (*TMA*), L-ascorbic acid (*AA*) and total polyphenols (*TP*), of raspberry pulp were investigated at 70, 80, 90 and 100 ºC for 2 h. The changes in *a** (redness-greenness), chroma (*C**) and browning index (*BI*) color parameters followed a first-order reaction with activation energies of 39.39, 35.60 and 51.17 kJ mol^{-1}, respectively. The degradation of *TMA* and *AA* also followed first order kinetics while *TP* did not show significant variations with thermal treatment. The activation energies of the *TMA* and *AA* changes were 28.36 and 29.47 kJ mol^{-1}, respectively. In addition, the activation energies revealed that *BI* was the most sensitive parameter towards temperature changes, while the reaction rate constants (*k*) showed that *AA* had the highest degradation

rate in comparison with the other parameters studied. The degradation of *TMA* showed a strong positive correlation with *a**. The results obtained in this study may be useful to food processors for designing and optimizing thermal treatment conditions in order to obtain high quality raspberry pulp products.

Keywords: Raspberry pulp, Thermal degradation kinectic, Color, Antocyanins, Polyphenols, Ascorbic acid

1. Introduction

Raspberry (*Rubus idaeus*), a member of the Rosaceae family, has attracted great interest owing not only to its good flavor and attractive color but also to its abundance of bioactive compounds, which have been shown to have beneficial effects on health (Si et al., 2016). However, due to the short shelf-life of raspberries, they must be frozen, or processed into products such as juices, pulps, jams, jellies, etc., and then be subjected to thermal processes (sterilization, pasteurization, dehydration, etc.). These processes are useful for extending the life and conservation period of food (Lespinard et al., 2012), but both the beneficial and the destructive consequences of heat need to be taken into account (Lespinard et al.,2015). Thus, major problems have to be confronted in the production of raspberry pulp, including operations which may affect their properties.

Color is the major attribute associated with the quality of berries and berry pulps, with the preservation of natural color pigments in thermally processed foods being a major challenge in food processing (Ahmed and Ramaswamy, 2005). Although the color of raspberry fruits is not significantly affected by freezing and cold storage, upon being crushed most fruit berries yield a highly pectinous pulp and release little free run juice

with poor color stability on storage or thermal processing (Ochoa et al., 1999). This color deterioration in berries has been described as a loss in redness.

Anthocyanins, which are responsible for the color in most berries, easily degrade following various reaction mechanisms affected by several factors such as pH, temperature, light, oxygen, and enzymes (Castañeda-Ovando et al., 2009; Rubinskiene et al., 2005). Temperature is also known to have a deleterious effect on anthocyanins (Harbourne et al., 2008).

In addition to having high levels of anthocyanins, raspberries contain phenolic compounds and ascorbic acid that significantly contribute to their antioxidant and anticarcinogenic properties (Szajdek and Borowska, 2008). Similar to the anthocyanins, phenolic compounds and ascorbic acid can also be degraded through heating.

Because of these fundamental health benefits, there is a need to preserve the content of anthocyanins, total phenolics and ascorbic acid in raspberries during thermal processing. For this reason, an accurate knowledge of the kinetic parameters, degradation rate constant and activation energy are essential to be able to quantitatively predict the changes in quality that occur during thermal processing. The optimization of thermal processing relies on the application of appropriate degradation kinetic models for safety and quality.

Despite there being a large amount of literature available on developed kinetic models such as zero-order, first-order and fractional conversion first-order for phytochemical content, antioxidant capacity, texture and color degradation for a range of fruit and vegetables, almost no attention has been devoted to raspberry pulp. Only Summen and Erge (2012) have reported the effect of heating on the degradation of bioactive compounds and color loss in raspberry pulp at different temperatures from 60 to 90°C for

7 hours. However, these authors considered regular one-hour sampling times to develop the kinetics, not evaluating shorter processing times which are required for the pasteurization of an acid product such as raspberry pulp.

On the other hand, the visual color, which is an indicator of pigment concentration, can be measured instantaneously using tristimulus colorimeters for on-line quality control (Ahmed et al., 2004). In this regard, Ahmed et al. (2004) found that a linear relationship described well the variation of total visual color with anthocyanin content of plum puree during thermal processing. Similarly, Kaur et al. (2006) found a direct relationship between visual color and lycopene content in tomato peel. Ahmed et al. (2000) have reported similar observations on dependence of total color on chlorophyll content of green chilli puree during thermal processing. Thus, the aforementioned could be useful to estimate the variation of anthocyanin content in raspberry pulp during thermal processing by using simple and fast online color measurement. However, studies relating anthocyanin content and color variations in raspberry pulp are still lacking.

Based on the above, the aims of this study were to determine the degradation kinetics of bioactive compounds and color, and to develop a relationship between color and anthocyanin in raspberry pulp during heat treatment, considering the time-temperature conditions required for pasteurization of this type of product.

2. Materials and methods

2.1. Preparation of raspberry pulp samples

Commercial maturity stage raspberries (*Rubus idaeus var. Autumn Bliss*, 25 kg with a rich purple red color), were provided by the Yuco Frutos establishment of Tío Pujio,

Córdoba (Argentina). The fresh fruits were transported to the laboratory, where they were frozen and stored at -20 °C until processing. For each isothermal experiment, about 500 g of frozen raspberries were thawed overnight (12 h) at 4 °C and then washed with tap water to remove superficial dirt. Afterwards, the raspberries were crushed to pulp using a domestic mixer (Smartchef, Peabody, Argentina). The pulp obtained in this way was used to evaluate the initial condition or zero time of each kinetic study. The samples were treated in darkness in a closed container to protect the photosensitive antioxidant compounds from degradation.

2.2. Thermal processing of pulp

Heat treatments were carried out at different temperatures (70, 80, 90 and 100 °C) for 0–120 min. Aliquots of 3 mL of raspberry pulp were put into screw-cap glass test tubes (i.d. 15 mm). Then the tubes were heated in a thermostatic water bath at a specified temperature, with an accuracy of ± 1°C, for preset times (0, 2, 5, 10, 20, 30, 60, 90 and 120 min). A thermocouple was placed in 3 tubes through the cap to monitor the temperature inside the tubes during heating. The time taken to reach the required heating temperature (come up time) was less than a minute and this time period was excluded from the kinetic parameter analysis. After the thermal treatment, the tubes were cooled down quickly in an ice-cold water bath to stop any further thermal degradation.

2.3. Color determination

The heat-treated pulp samples were homogenized by vortexing and then placed in a ceramic cell (3 cm in diameter) for color determination; which was carried out using a colorimeter (Konica Minoltta CR-400, Tokyo, Japan) with a measuring area of 8 mm in

diameter and provided with a 10° standard observer and a D65 standard illuminant. The determination was based on the CIELab color space made up of three colorimetric coordinates, L^*, a^* and b^*. The value of L^* means lightness (0 for black and 100 for white), the value a^* represents greenness and redness (negative values for green, positive values for red) and the value b^* shows the variation between bluish and yellowish colors (negative values for blue, positive values for yellow). The instrument was calibrated with a standard white plate (sY=93.2, sx=0.3133, and sy=0.3192) and each color determination was made in triplicate.

From the CIELab coordinates obtained, the colorimetric indexes chroma (C^*) and browning index (BI) were calculated using the Eqs. (1) and (2), respectively:

$$C^* = [(a^*)^2 + (b^*)^2]^{1/2} \quad (1)$$

$$BI = 100\,(X - 0.31)/0.17 \quad (2)$$

where

$$X = (a^* + 1.75\,L^*) / (5.645\,L^* + a^* - 3.012\,b^*) \quad (3)$$

2.4. Total monomeric anthocyanin content

Anthocyanins were extracted from raspberry pulp samples using the mixture of solvents: acetone/water (70:30) acidified 0.1% HCl according to Giusti and Wrolstad (1996) protocol. For the extraction 1 g of pulp was mixed with 5 mL acetone/water for 3 min by vortex and centrifuged at 5,960.28 RCF for 10 minutes at 4 °C. The obtained supernatant was recovered, and then a second extraction was carried out. Both the supernatants were collected for measurement. The total monomeric anthocyanin (TMA) content was determined using a pH differential method reported by Giusti and Wrolstad (2005). A UV-VIS spectrophotometer with a diode array (Analitik jena specord S600, Jena,

Germany) and disposable cuvette with a 1 cm optical path (*l*) were used for the determinations. The anthocyanin pigment content was calculated as cyanidine-3-glucoside, using a molar extinction coefficient (ε) of 26900 cm^{-1} mg^{-1} and a molecular weight (*MW*) of 449.2 g mol^{-1}, according to Giusti and Wrolstad (1996). The absorbance was measured at 520 nm (A^{520}) and 700 nm (A^{700}), and all samples were analyzed in triplicate. The *TMA* content was expressed as mg cyanidin-3-glucoside equivalents per 100 g fresh weight (fw) of raspberry pulp and calculated as follows:

$$TMA = (A\ V_e\ MW\ FD\ 10^2) / (\varepsilon\ l\ W_s) \quad (4)$$

where *A* is the absorbance, *Ve* is the extraction volume, *FD* is the dilution factor, ε is the molar extinction coefficient, *l* is the path length of the cuvette and *Ws* is the sample weight.

Absorbance was calculated by the following Eq.5:

$$A = (A^{520} - A^{700})_{pH1} - (A^{520} - A^{700})_{pH4.5} \quad (5)$$

2.5. L-ascorbic acid content

The measurement of L-ascorbic acid (*AA*) was performed by HPLC according to a procedure described by Tiwari et al. (2009) with minor modifications. First, 1 g of pulp was mixed in a 15 mL centrifugal tube with 5 mL of 2.5% (w/v) metaphosphoric acid (Merck, Darmstadt, Germany), after which the sample was mixed for 3 min with vortex and protected from light. This was centrifuged at 5,338.78 RCF for 10 min at 4 °C, and then the extract was filtered through a 45 μm nylon filter (GVS Filter Technology, USA) and placed in a 1 mL eppendorf tube protected from the light. Finally, 20 μl of filtered extract were injected into the HPLC. The chromatographic system used consisted of an

HPLC (Thermo Scientific ULTIMATE 3000, USA) with quaternary pump, and C18 column (150 x 4.6 mm, 5 μm, PRONTOSIL SPHERIBOND ODS2, Germany). A DAD detector was used at a wavelength of 245 nm. The mobile phase consisted of a 93:7 mixture of 0.5% w/v metaphosphoric acid and acetonitrile (ACN) (pH:2), which was isocratically pumped at 1 mL min^{-1}. Chromatograms were processed using the Thermo Scientific Chromeleon Chromatography Data System (CDS) software. The results were calculated using the L-ascorbic acid standard curve and the areas obtained in the chromatograms. All samples were analyzed in triplicate, and the results were expressed as mg L-ascorbic acid (Sigma-Aldrich, Saint Louis, USA), (*AA*)/100 g fresh weight.

2.6. Total phenolic content

The concentration of total polyphenols was determined by the Folin-Ciocalteu colorimetric method, with gallic acid as a calibration standard, as described by Kim and Padilla-Zakour (2004) with modifications. First, the bioactive components were extracted using the same mixture of solvents as used to determine the anthocyanins (section 2.4), according to Giusti and Wrolstad (1996). First, 1 g of pulp was mixed with 2 mL of acetone/water for 3 min by vortex and centrifuged at 5,338.78 RCF for 10 min at 4 °C, after which, the obtained supernatant was recovered and 5 extractions were made and combined for the measurement of total polyphenols. An aliquot of 50 μl of extract and 800 μl of distilled water were mixed in a tube protected from light. Then, 125 μl of Folin-Ciocalteu (Merck, Darmstadt, Germany) reagent were added, and the mixture was stirred by vortex and left to stand for 3 min. Finally, 125 μl of 20% (w/v) sodium carbonate was added and mixed again. After incubation for 90 min at 25 °C in constant agitation (Thermo Scientific MAXQ 4450 orbital shaker, Waltham, Massachusetts, USA) and

darkness, the absorbance was read against the target prepared at 765 nm. The total polyphenolic content of raspberry pulp was expressed as mg gallic acid (Sigma-Aldrich, Saint Louis, USA) equivalents per 100 g (mg GAE/100 g) fresh weight (fw) of raspberry pulp. All samples were analyzed in triplicate.

2.7. Mathematical models and kinetic analysis

The degradation kinetic of raspberry pulp color change, anthocyanins content, total polyphenols content and L-ascorbic acid content were evaluated by means of two kinetic models, zero order (Eq.6) and first order (Eq.7). To estimate the parameters, the mean values of the determinations carried out in triplicate were used.

$$C = C_0 - kt \tag{6}$$

$$C/C_0 = exp\,(-kt) \tag{7}$$

Where C is the parameter to be estimated, C_0 indicates the value of the parameter in the initial condition, t is the thermal processing time, and k is the rate constant at temperature T.

The half-life ($t_{1/2}$) of the degradation reaction was calculated assuming the first-order kinetics according to Eq.8:

$$t_{1/2} = ln2/k \tag{8}$$

The k temperature dependence was modeled using Eq.9 through an Arrhenius-type relationship, obtaining the activation energy (E_a) which is normally used to describe the energy required to reach the transition state of a reaction (Lodish et al., 2000). The

Arrhenius equation has been widely used as a model of the temperature effect on the rate of chemical reactions and biological processes in foods (Peleg et al., 2012).

$$k = k_0 \exp(-E_a/RT) \quad (9)$$

Where k_0 is the frequency factor, E_a is the activation energy, R is the universal gas constant (0.00831 kJ mol^{-1} K^{-1}), and T is the absolute temperature. For parameter estimation, individual measures were used instead of mean values of triplicates, thus taking into account variability within the samples.

2.8. Statistical analysis

Experimental determinations were performed in triplicate. The results were expressed as mean values ± standard deviation. All data were adjusted to the model using Microsoft® EXCEL software version 2010. The statistical analysis of the data was based on the analysis of variance (ANOVA). The statistically significant differences between the means were evaluated by Fisher's test and the relationship between the color parameter a* and anthocyanin was determined by Pearson's test, using INFOSTAT statistical software version 2017 (Facultad de Ciencias Agrarias, Universidad Nacional de Córdoba, Argentina). Values of $P<0.05$ were considered statistically significant. The determination coefficient (R^2) was used as the model fit criterion.

3. Results and discussion

3.1. The effect of thermal processing on color

Fresh raspberries presented an intense purple red color with an average luminosity, as indicated by the CIElab parameters values obtained: a^* was 33.46±1.6, b^* was 13.68±0.86 and L^*, related to luminosity, was 35.21±1.43 with a *BI* of 116.31±1.74 and a *C** of 36.16±1.79. Fig. 1 shows the effect of temperature on the a^*, *BI* and *C** values of raspberry pulp. As can be observed, the heating had an adverse effect on color based on the zero order and first order kinetic models. Although some linearity in the evolution of color parameters was observed for some temperatures, from the comparison of fits between the zero and first order models, the latter revealed to be the most suitable with R^2 values of between 0.90 and 0.99. The results obtained for the *a**, *BI* and *C** parameters variations have been modeled, while no kinetic model was found to describe adequately the changes in *L** and *b** for the different temperatures and times studied (data not shown). Kinetic parameters, including kinetic rate constant (k) and half-life ($t_{1/2}$), were calculated from the C/C_0 vs. time curves (Fig. 1) and are presented in Table 1. As expected, the k values increased with temperature, indicating that a greater degradation occurred at higher processing temperatures. The k values for the changes in *a**, *BI* and *C** during heating ranged between 6–19 x 10^{-4} min^{-1}, 8–22 x 10^{-4} min^{-1} and 7–32 x 10^{-4} min^{-1}, respectively. Similarly, Nisha et al. (2011) indicated that the loss of red color in heat-treated tomato puree followed first order reaction kinetics at 50-120 ºC. They found similar k values for the redness color degradation (a_t/a_0) as 10^{-4} and 19 x 10^{-4} min^{-1} at 70 and 100 ºC, respectively. In addition, in a study by Patras et al. (2011), the rate of color change in strawberry jam during storage was also observed to follow first-order reaction kinetics.

The *a** values for raspberry pulp heat-treated at 70, 80, 90 and 100 °C for 120 min, showed a decrease of 6.50, 8.20, 11.27 and 20.72%, respectively. For parameters *BI* and

*C**, the decrease was 7.90, 9.70, 16.06, 29.81% and 7.97, 9.56, 12.15, 22.67%, respectively. From Fig. 1 it can be observed that the color parameters decreased with treatment time, with this reduction accelerating when temperature increased. The kinetic parameters obtained for *a**, *BI* and *C** did not present any significant differences ($P>0.05$) between treatments at 70 and 80 °C. However, significant differences ($P<0.05$) were found between thermal treatments at 80, 90 and 100 °C.

To evaluate the effect of temperature on the kinetic constants, the data shown in Table 1 were adjusted to the Arrhenius equation (Eq.9), with Table 2 displaying the fit results for *a**, *BI* and *C**. The activation energy (E_a) is a measure of the effect of temperature on each of the processes. For the same temperature increase, the higher the value of the activation energy, the higher is the effect it produces. Therefore, the browning index (*BI*) was the most affected by the temperature increase, followed by *a** and finally chroma (*C**), with values of 51.17, 39.39 and 35.60 kJ mol^{-1}, respectively (Table 2). Related to this, these values are much lower than those found by Summen & Erge (2012), who reported values of activation energy in raspberry pulp of 75.5 and 67.1 kJ mol^{-1} for *a** and *C**, respectively. This difference between the activation energies of both works could be due to the fact that these authors carried out the kinetic study by taking the first sample one hour after the start of heating. Thus, they omitted the first hour of heating, where the highest variations of color occur. This fact could affect the *k* value obtained differently for each temperature (varying this affectation with temperature) and consequently the activation energy. On the other hand, the range of temperatures studied in both works were slightly different (60-90°C and 70-100°C), which may also explain the differences in the E_a values.

The E_a values obtained in current study are similar to that found by Ahmed et al. (2002) for color degradation in papaya puree, who reported a value of 32.59 kJ mol^{-1}. Ahmed et al. (2004) obtained an E_a value of 27.78 kJ mol^{-1} for the a^* coordinate in thermally treated plum puree, which was slightly lower than the one obtained in the present study, indicating that raspberry pulp is more sensitive to temperature changes than plum puree.

3.2. Thermal degradation of total monomeric anthocyanin

The concentration of anthocyanin in raspberry pulp decreased with heat treatments. Initially at zero time, the raspberry pulp had an average concentration of 30.84±3.79 (mg 100 g^{-1}fw), with similar values of 35.1±2.6 and 39.1±6.8 (mg 100 g^{-1}fw) being reported by Pantelidis et al. (2007) for raspberry anthocyanin concentrations. Ochoa et al. (1999) reported values between 19.40 and 28.89 (mg 100 g^{-1}fw), for different raspberry cultivars. The results showed that heating had an adverse effect on anthocyanin content for all conditions studied at 70, 80, 90 and 100 °C, with this decreasing as process time and temperature increased (Fig. 2). This decrease found in anthocyanin content, for different temperatures and process times, was evaluated by zero order and first order kinetic models. It was shown that the first-order kinetic model (Eq.7) was adequate for representing the effect of heat treatment on the anthocyanin degradation of raspberry pulp, as can be observed in Fig. 2. The coefficient of determination (R^2), presented in Table 1, ranged from 0.961 to 0.998, which indicates the goodness of fit of the first order kinetic model to the experimental data.

Other studies in fruits have reported first-order kinetics for the degradation of anthocyanin, including Cisse et al. (2009) for thermal degradation of blood orange,

blackberry and roselle, Patras et al. (2011) for strawberry jam during storage, Ochoa et al. (1999) for raspberry pulp during storage. Moreover, in cereals such as black rice, the anthocyanins were shown to present the same mechanism of thermal degradation (Hou et al., 2013).

The percentage decrease of anthocyanin in raspberry pulp heat treated for 120 min was 24.77, 26.35, 33.62 and 46.08% for 70, 80, 90 and 100 °C, respectively (Fig. 2), with $t_{1/2}$ values varying from 297.7 to 134.5 min for the temperature range studied. Temperature dependence of anthocyanin degradation was determined by Arrhenius equation (Eq.9). The reported applications of the Arrhenius model have not been restricted to the rates of simple chemical reactions such as vitamin degradation (Peleg et al. 2012). Anthocyanin degradation, and consequently also the color development, are due to complex reactions, where different serial steps and various intermediate compounds are formed depending on anthocyanin structure (Cisse et al., 2009) as well as nature and severity of heating (Patras et al., 2010). Therefore, the problem could arise when the reaction does not follow a fixed order kinetic (Peleg et al., 2012), but this is not the case in the present study since the processes follow a fixed order kinetic showing good correspondence with the Arrhenius model to describe the k-dependence with temperature. Thus, the activation energy for anthocyanin degradation was calculated as 28.36 kJ mol^{-1} and determination coefficient (R^2) of Arrhenius plot was 0.92. These results are similar with the results of Tanchev (1972), who found values between 22.2-24.9 kJ mol^{-1} for the thermal degradation of anthocyanin in raspberry juice. Cisse et al. (2009) reported a value of 37.23 kJ mol^{-1} for thermally treated blackberry pulp. Summen and Erge (2012) reported a higher activation energy value of E_a=49 kJ mol^{-1} in thermally treated raspberry pulp. This difference could be due to the different temperature ranges studied and to the times at

which the samples were analyzed in both investigations, as discussed above for color. Related to this, Martynenko and Chen (2016) showed that E_a for anthocyanin degradation in blueberries juice varied depending on the temperature range considered. Furthermore, as stated by Deylami et al. (2016), even talking about anthocyanins from the same fruit, the degradation strongly depends, and consequently also the activation energy, on physicochemical characteristics such as pH, solid content and the presence of other compounds such as sugars and polyphenols.

Although the kinetic parameters obtained did not present significant differences for thermal treatments at 70 and 80 °C, at higher temperatures significant differences were noted ($p<0.05$), as observed in Table 1 for thermal treatments at 80, 90 and 100 °C. A similar effect was obtained for the color change, and this correlation in the results suggests that anthocyanin degradation is predominantly responsible for the color changes observed in raspberry pulp.

3.3. Thermal degradation of L-ascorbic acid

The mean initial concentration of L-ascorbic acid in raspberry pulp was 11.54±0.58 (mg 100 g^{-1} fw). Skrovankova et al. (2015) reported a range of 5-40 (mg 100 g^{-1} fw) for the concentration of L-ascorbic acid in fresh raspberry, with similar values being reported by Ochoa et al. (1999), who found values of between 16.12 and 28.89 (mg 100 g^{-1}fw) depending on the raspberry cultivar. However, Pantelidis et al. (2007) obtained higher values of ascorbic acid content in autumn raspberry cultivars an ascorbic acid content of between 31.0 and 40.0 (mg 100 g^{-1} fw), while spring raspberry contained between 16.8 and 37.7 (mg 100 g^{-1} fw). In this sense, Skrovankova et al. (2015) stated that the variation

of the L-ascorbic acid content is related to the varieties of cultivars, environmental factors acting on the crop, storage conditions of the fruit and also due to characteristics of the compound related to its instability and sensitivity to light, heat and oxygen. The results obtained from the thermal treatments at 70, 80, 90 and 100 °C indicated an adverse effect on the L-ascorbic acid content, with the concentration decreasing as the temperature and processing time increased.

The thermal degradation of L-ascorbic acid, for different temperatures and process times, was evaluated by zero order and first order kinetic models. The first-order kinetic model (Eq.7) was found to be the most suitable for representing the effect of thermal degradation of L-ascorbic acid in raspberry pulp, as shown in Fig. 3. Other studies on fruits also applied first-order kinetics to represent the thermal degradation of L-ascorbic acid; Ochoa et al. (1999) reported first-order kinetics in raspberry pulp during storage, as well as Garzón and Wrolstad (2002) in strawberry juice and concentrates. Also, for ground cashew apples at high temperatures, Lima et al. (2010) reported the same degradation kinetics.

As shown in Fig. 3, thermal degradation of L-ascorbic followed a first order reaction kinetics. High correlation coefficients (0.928-0.99) between the experimental and predicted values were obtained at all four levels of the applied temperature, indicating the suitability of the kinetic model. The percentage decrease of L-ascorbic acid during heat treatment for 120 min was 40.60, 47.68, 61.59 and 66.44% for 70, 80, 90 and 100 °C, respectively (Fig. 3). These results revealed the higher thermal instability of L-ascorbic acid, with respect to the other quality components evaluated, since the decrease obtained at 70 °C of 40.60% was similar to that obtained of 46.08% at 100 °C in anthocyanin. On

the other hand, the percentage decrease of L-ascorbic acid at 70 °C was significantly higher than the change produced on the colorimetric parameters at 100 °C.

The kinetic parameters obtained showed significant differences ($p<0.05$) for all the thermal treatments studied (70, 80, 90 and 100 °C, see Table 1), while for anthocyanin and color significant differences were observed starting from 80 °C. This further supports the claim that L-ascorbic acid has higher thermal instability compared to the other components evaluated in raspberry pulp.

The effect of temperature on the kinetic constants was evaluated by the Arrhenius equation (Eq.9), with Table 2 showing Arrhenius parameters with an R^2=0.958. The activation energy obtained was 29.47 kJ mol^{-1}, similar to anthocyanin but lower than the activation energy of the colorimetric parameters. Similar activation energy values have been reported for L-ascorbic acid in other fruit pulps, such as thermally treated strawberry, mango and marula pulps, which showed activation energies of 21.36, 39 and 29 (kJ mol^{-1}), respectively (Castro et al., 2004; Hiwilepo-van Hal et al., 2012).

3.4. Evolution of total polyphenols during heat treatment

The total polyphenols had an initial mean concentration of 184.96±5.94 (mg 100 g^{-1} fw). Other authors have reported similar values for raspberry, with De Ancos et al. obtaining a total polyphenol content of 113.72-177.60 (mg 100 g^{-1} fw), and values of between 104±1.5 and 245±6.1 (mg 100 g^{-1} fw) being reported for *Autumn Bliss* variety raspberries by Wang and Lin (2000). On the other hand, higher contents of total polyphenols 341.5±21.8 (mg 100 g^{-1} fw) was reported by Kim and Padilla-Zakour (2004). These

differences found in total polyphenol content are related to raspberry variety and the growing conditions (Connor et al., 2019; Skrovankova et al., 2015).

Fig. 4 shows the evolution of total polyphenols in raspberry pulp for different heat treatments, where it can be observed that for the heat-treated pulp there were no significant differences between the initial total polyphenol contents and those resulting from heat treatment at different temperatures. Contrasting results have been reported regarding what occurs after heat treatment with the content of total polyphenols in various foods. An increase in the content of total polyphenols was observed in grape, plum, quince and quince jam, black carrot jam, and red beet jam (Baroni et al., 2018; Guldiken et al., 2016; He et al., 2016; Kamiloglu et al., 2015; Miletić et al., 2013), possibly due to alteration and rupture of cell walls and the thermal degradation of complexes with protein (Baroni et al., 2018; Cilla et al., 2018). However, a decrease in total polyphenol content was observed in beet, plum and cabbage pickles and milk-based fruit drinks (Cilla et al., 2012; Guldiken et al., 2016; Kaulmann et al., 2016), probably due to the thermal degradation of compounds outside a protective matrix.

Raspberry pulp, due to its different characteristics with respect to the whole fruit and a juice, presents an evolution of the total polyphenol content during the thermal treatment, which may be explained by the two mechanisms of release and thermal degradation occurring simultaneously, causing an apparent stability.

3.5. Relationship between value a and total monomeric anthocyanin content*

The red color represented by the co-ordinate *a** is related to the anthocyanin content, the most abundant pigment in raspberries (Patras et al., 2010; Summen and Erge, 2012). Due

to this relationship, sensory changes were revealed when evaluating the decrease of *a** during thermal processing, and indirectly this suggests composition changes taking place in the raspberry pulp, with this relationship also being observed by Bustos et al. (2018). Fig. 5 shows a strong positive correlation between the anthocyanin content variation and the loss of red color represented by the value of *a** in thermally treated raspberry pulp. This ratio was evaluated by the Pearson coefficient, with a value of r = 0.930 being obtained. In order to obtain a predictive index to estimate the losses by thermal degradation of anthocyanin by measuring the value of *a**, the relationship between the variation of both parameters was adjusted by linear regression (R^2=0.87), and was given by the following linear equation:

$$y = 2.35\ x\ -1.36 \quad (10)$$

where *y* is the relative loss of anthocyanin and *x* the relative variation of value *a**, with respect to initial values during heat treatment. These results suggest that the colorimetric co-ordinate *a** can be used as a good indicator for anthocyanin degradation in raspberry pulp during thermal processing within the temperature range evaluated in this study (70-100°C).

4. Conclusions

This study aimed at determining the kinetics of thermal degradation of color and bioactive compounds in raspberry pulp. The first-order kinetic model was found to be the best fit for color, anthocyanins and ascorbic acid degradation, with the effect of temperature on the degradation rate constants being adequately described by the Arrhenius. The activation energies revealed that *BI* was the most sensitive parameter towards temperature changes, while the values of the reaction rate constants (*k*) showed that L-ascorbic acid

had the highest degradation rate in comparison with the other parameters studied. The degradation of total anthocyanins revealed a strong positive correlation with a^*. Thus, it can be inferred that visual color measured instantaneously by tristimulus colorimeters for on-line quality control, could be used to predict the anthocyanins degradation during thermal processing of raspberry pulp at temperatures between 70 and 100°C. The results obtained in this study may be useful for optimizing the pasteurization process of raspberry pulp, in order to minimize the loss of color and bioactive components. As a perspective, the kinetic models developed can be coupled to a heat transfer model, to include quality aspects into the simulation of thermal processing of raspberry pulp. In conclusion, this work presents kinetic models which can be used by food processors and engineers in order to design and optimize thermal treatment conditions to obtain high quality raspberry pulp products.

Declaration of interests

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Figure Captions

Fig. 1. Isothermal degradation of *a** (A), *BI* (B) and *C** (C) in raspberry pulp, treated at different temperatures [70 °C (■), 80 °C (▲), 90 °C (X) and 100 °C (◆)]. The lines represent model fits (Eq.7) to experimental data. Bars represent mean ± standard deviation.

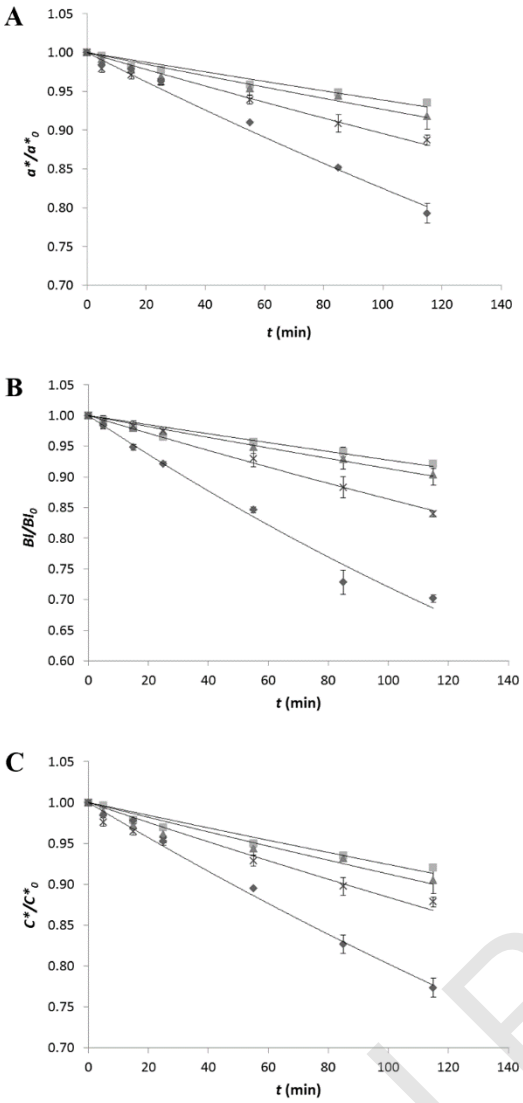

Fig. 2. Isothermal degradation of total monomeric anthocyanin (*TMA*) content in raspberry pulp, treated at different temperatures [70 °C (■), 80 °C (▲), 90 °C (X) and 100 °C (◆)]. The lines represent model fits (Eq.7) to experimental data. Bars represent mean ± standard deviation.

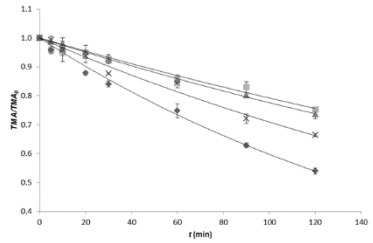

Fig. 3. Isothermal degradation of L-Ascorbic Acid (*AA*) in raspberry pulp, treated at different temperatures [70 °C (■), 80 °C (▲), 90 °C (X) and 100 °C (◆)]. The lines represent model fits (Eq.7) to experimental data. Bars represent mean ± standard deviation.

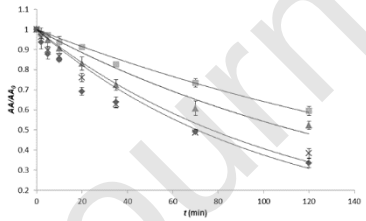

Fig. 4. Evolution of the content of total polyphenols (*TP*) in raspberry pulp with treatment time, at different temperatures [70 °C (■), 80 °C (▲), 90 °C (X) and 100 °C (◆)]. Bars represent mean ± standard deviation.

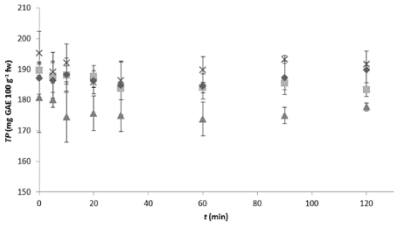

Fig. 5. Relationship between relative loss of total monomeric anthocyanin (*TMA*) and relative variation of value *a**, with respect to the initial concentration during heat treatment. The line represents the behavior predicted by the lineal model (Eq.10). Bars represent mean ± standard deviation.

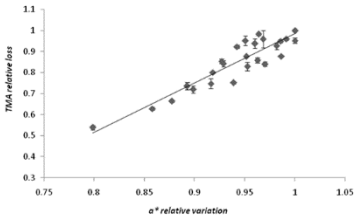

Table 1 kinetic parameters (*k*) and coefficient of determination (R^2) of color loss and bioactive compounds degradation in raspberry pulp heat-treated at different temperatures[z]

	T **(°C)**	***k x 10^{-3}*** **(min^{-1})**	**R^2**	***$t_{1/2}$*** **(min)**
*a**	70	0.6±0.0[a]	0.94	1100.4±17.5
	80	0.8±0.1[a]	0.92	922.0±139.6
	90	1.1±0.1[b]	0.94	630.6±46.8
	100	1.9±0.1[c]	0.99	360.2±16.1
*C**	70	0.8±0.0[a]	0.94	879.1±15.7
	80	0.9±0.1[a]	0.91	764.9±100.0
	90	1.2±0.1[b]	0.92	536.8±39.0
	100	2.2±0.1[c]	0.99	316.2±17.7
BI	70	0.7±0.1[a]	0.92	924.7±79.6
	80	0.9±0.2[a]	0.98	783.7±147.5
	90	1.5±0.1[b]	0.99	475.9±40.2
	100	3.2.±0.2[c]	0.99	215.5±15.7
Total Monomeric Anthocyanin	70	2.3±0.1[a]	0.96	297.7±17.5
	80	2.5±0.1[a]	0.99	273.7±13.1
	90	3.4.±0.2[b]	0.98	201.8±9.1
	100	5.2±0.1[c]	0.99	134.5±3.4

L-AscorbicAcid	70	4.4.±0.3[a]	0.99	156.4±10.8
	80	6.1±0.3[b]	0.92	113.4±6.4
	90	9.0±0.3[c]	0.93	77.2±2.7
	100	9.8±0.6[d]	0.94	70.8±4.0

[z]Within the same parameter, values with different letters indicate significant differences between heat treatments ($P< 0.05$).
±Standard deviation.

Table 2 Parameters of Arrhenius equation and coefficient of determination (R^2) for color and bioactive compounds in raspberry pulp

	***ln k*$_0$ (min^{-1})**	***Ea* (kJ mol^{-1})**	**R^2**
*a**	6.35±1.25	39.39±3.74	0.94
*C**	5.23±1.19	35.60±3.54	0.91
BI	10.62±0.98	51.17±2.94	0.91
Total Monomeric Anthocyanin	3.80±0.91	28.36±2.77	0.92
L-AscorbicAcid	4.95±1.09	29.47±3.24	0.96